## Ludwig Boltzmann – A Pioneer of Modern Physics <sup>1</sup>

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In two respects Ludwig Boltzmann was a pioneer of quantum mechanics. First because in his statistical interpretation of the second law of thermodynamics he introduced the theory of probability into a fundamental law of physics and thus broke with the classical prejudice, that fundamental laws have to be strictly deterministic. Even Max Planck had not been ready to accept Boltzmann's statistical methods until 1900. With Boltzmann's pioneering work the probabilistic interpretation of quantum mechanics had already a precedent. In fact in a paper in 1897 Boltzmann had already suggested to Planck to use his statistical methods for the treatment of black body radiation.

The second pioneering step towards quantum mechanics was Boltzmann's introduction of discrete energy levels. Boltzmann used this method already in his 1872 paper on the *H*-theorem. One may ask whether Boltzmann considered this procedure only as a mathematical device or whether he attributed physical significance to it. In this connection Ostwald reports that when he and Planck tried to convince Boltzmann of the superiority of purely thermodynamic methods over atomism at the Halle Conference in 1891 Boltzmann suddenly said: "I see no reason why energy shouldn't also be regarded as divided atomically."

Finally I would like to mention, that Boltzmann in his lectures on Natural Philosophy in 1903 already anticipated the equal treatment of space coordinates and time introduced in the theory of special relativity. Furthermore in the lectures by Boltzmann and his successor Fritz Hasenöhrl in Vienna the students learned already about noneuclidean geometry, so that they could immediately start to work when Einstein's general theory of relativity had been formulated.

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Before 1900 classical Newtonian mechanics was the prototype of a successful physical theory. As a consequence all physical laws had to be strictly deterministic and universally valid. For most physicists – among them Max Planck – these rules applied also to thermodynamics. They believed that the second law of thermodynamics was a basic axiom handed down from God, which one had to accept as the starting point of any thermodynamic consideration. In contrast to this view was Boltzmann's statistical interpretation of the second law of thermodynamics which he first formulated in 1877, nearly 50 years before the statistical interpretation of quantum mechanics. Ludwig Boltzmann was born in Vienna in 1844 and died in Duino near Trieste in 1906. He studied mathematics and physics at the University of Vienna from 1863 to 1866, where Josef Stefan was his main advisor. He discussed a lot with his senior friend Josef Loschmidt.

Boltzmann for the first time introduced the theory of probability into a fundamental law of physics and thus broke with the classical prejudice, that fundamental laws of physics have to be strictly deterministic. Because of this prejudice it is no wonder that in the last decades of the 19th century Boltzmann's statistical interpretation of thermodynamics was not accepted by the physics community but met with violent objections coming from physicists and mathematicians. These objections were formulated in the form of paradoxes. The most prominent objections were the reversibility paradox by Boltzmann's friend Josef Loschmidt<sup>2</sup> in 1876 and the recurrence paradox by E. Zermelo<sup>3</sup> in 1896. Boltzmann met these objections by statistical arguments. This struggle for Boltzmann's ideas, however, helped to pave the way for the statistical interpretation of quantum mechanics in 1926 by Max Born. Boltzmann's expression for the entropy formulated in his paper of 1877 entitled "On the relation between the second law of the mechanical theory of heat and the probability calculus with respect to the theorems on thermal equilibrium"<sup>4</sup>, is a probabilistic expression. He found that for a closed system the entropy S of the system is proportional to the phase space volume  $\Omega$  occupied by the macrostate of the system  $S \propto \log \Omega$ . Furthermore Boltzmann already introduced finite cells in phase space. Using such cells to count the number of microstates this formula is now usually written in the notation of Max Planck  $S = k \log W$ . It implies that the entropy S is proportional to the logarithm of the so called thermodynamic probability W of the macrostate. W is actually the number of microstates by which the macrostate of the system can be realized. A macrostate is determined by a rather small number of macroscopic variables of the system such as volume, pressure and temperature. The latter two correspond to averages over microscopic variables of the system. A microstate, on the other hand, is specified by the coordinates and momenta of all molecules of the system. Due to the large number of molecules there is a very large number of different choices for the individual coordinates and momenta which lead to the same macrostate. For a closed system every microstate

<sup>&</sup>lt;sup>2</sup>J. Loschmidt: "Uber den Zustand des Wärmegleichgewichtes eines Systems von Körpern mit Rücksicht auf die Schwerkraft, 1. Teil, Sitzungsber. Kais. Akad. Wiss. Wien Math. Naturwiss. Classe **73** (1876) 128–142.

<sup>&</sup>lt;sup>3</sup>E. Zermelo: "Uber einen Satz der Dynamik und die mechanische Wärmetheorie, Ann. Physik **57** (1896) 485–494.

<sup>&</sup>lt;sup>4</sup> L. Boltzmann: Über die Beziehung zwischen dem Zweiten Hauptsatze der mechanischen Wärmetheorie und der Wahrscheinlichkeitsrechnung resp. den Sätzen über das Wärmegleichgewicht, Sitzungsber. Kais. Akad. Wiss. Wien Math. Naturwiss. Classe **76** (1877) 373–435.

has the same a priori probability. If one divides W by the total number of microstates accessible to the system including those of all other possible macrostates one obtains the normalized probability to find a closed system just in this macrostate. It turns out, that the largest number of microstates corresponds to the state of thermodynamic equilibrium which thus is the state of maximal entropy just as required by the second law of thermodynamics.

Futhermore Boltzmann could show that for a very large system, by far the largest number of all microstates corresponds to equilibrium—and quasi-equilibrium—states. The latter are states which differ very little from the equilibrium state with maximum entropy and cannot be distinguished macroscopically from the equilibrium state. As an example let us create a nonequilibrium state by pouring, for instance, a dye into a liquid. At first the dye will only be in a limited region, which corresponds to a nonequilibrium state, but it will gradually spread through the whole liquid. This behaviour is typical whenever you make such an experiment. It is easy to tell the sequence in which snapshots of a spreading dye were taken, even after their original order has been deranged. How does this unidirectional behaviour in time come about? In our example of a liquid containing a dye the equilibrium— and quasi-equilibrium states correspond to a practically uniform distribution of the dye through the whole liquid with very small intensity fluctuations of the dye. With increasing size of the system, the preponderance of the equilibrium- and quasi-equilibrium-states becomes even more overwhelming. If for every possible microstate of a large system we put a marked sphere into an urn and afterwards drew spheres from the urn indiscriminately, we would practically always draw an equilibrium or quasi-equilibrium state. The transition from nonequilibrium to equilibrium thus corresponds to a transition from exceptionally unprobable nonequilibrium-states to the extremely probable equilibriumstate. This is Boltzmann's statistical interpretation of the second law. The appearance of so-called statistical fluctuations in small subsystems was predicted by Boltzmann and he recognized Brownian motion as such a phenomenon. The theory of Brownian motion has been worked out independently by Albert Einstein in 1905 and by Marian Smoluchowski. The experimental verification of these theoretical results by Jean Baptiste Perrin was important evidence for the existence of molecules.

The second pioneering step which Boltzmann made towards quantum mechanics was the introduction of discrete energy levels for molecules contained in a finite volume. Boltzmann used this method already in his paper of 1872 on the H-theorem<sup>5</sup> and he needed it in the above mentioned paper of 1877 to be able to enumerate the number of microstates. Boltzmann actually introduced cells of finite size in phase–space spanned by the coordinates and momenta of all molecules. In quantum mechanics Heisenberg's uncertainty principle fixes the minimal size of such cells. Max Planck was certainly influenced by these ideas of Boltzmann.

In 1897 Boltzmann had a dispute with Planck on the irreversibility of radiation phenomena which may have stimulated Planck's discovery of quantum mechanics in 1900. At this time Planck thought that he could derive irreversible behaviour for

<sup>&</sup>lt;sup>5</sup>L. Boltzmann: Weitere Studien über das Wärmegleichgewicht unter Gasmolekülen, Sitzungsber. Kais. Akad. Wiss. Wien Math. Naturwiss. Classe **66** (1872) 275–370.

radiative processes without any assumptions on the initial states. Boltzmann could, however, show that this was not true and at the beginning of his second paper answering Planck<sup>6</sup> he made the following suggestion to Planck:

"It is certainly possible and would be gratifying to derive for radiation phenomena a theorem analogously to the entropy theorem from the general laws for these phenomena using the same principles as in gas theory. Thus I would be pleased, if the work of Dr. Planck on the scattering of electrical plane waves by very small resonators would become useful in this respect, which by the way are very simple calculations whose correctness I have never put in doubt.

Only if Dr. Planck in his second communication claims again that no other process in nature is known, in which conservative forces lead to irreversible changes, I can not agree."

Indeed Planck followed Boltzmann's recommendation and used Boltzmann's statistical methods for the derivation of his celebrated law for the black body radiation. Planck used thereby the additional assumption that classical oscillators absorb and emit energy only in integer multiples of the product of Planck's constant h with the frequency  $\nu$  of the radiation which gave rise to the birth of quantum mechanics. In fact, in the framework of Boltzmann's statistical approach it was quite common to introduce discrete energy levels to obtain a denumerable set of states. Boltzmann used this method already in his 1872 paper on the H-theorem<sup>7</sup>. One may ask whether Boltzmann considered this procedure only as a mathematical device or whether he attributed physical significance to it. In this connection Ostwald reports that when he and Planck tried to convince Boltzmann of the superiority of purely thermodynamic methods over atomism at the Halle Conference in 1891 Boltzmann suddenly said:

"I see no reason why energy shouldn't also be regarded as divided atomically." 8

At this time Planck was still an opponent of the atomistic theory. In 1900, however, he was converted from "Saulus" to "Paulus" when he had to use Boltzmann's statistical methods to explain his law of radiation and he became the most important proponent of Boltzmann's ideas. After Boltzmann's death in 1906 it was the authority of Max Planck and Albert Einstein which brought general recognition of Boltzmann's ideas. In the years 1909 and 1910, for instance, Planck had a vivid dispute with Ernst Mach on the existence of atoms. Without the concept of atoms it is very unlikely that quantum theory would have developed. The existence of atoms is one of the basic assumptions of Boltzmann's statistical mechanics for which he fought vigorously. In fact the deviations from the classical equipartition theorem for the energy observed for black body radiation and for the specific heat of solids were important evidence for quantum theory. Especially Erwin Schrdinger, the founder of wave mechanics, studied the applications of Boltzmann's statistical methods in great detail. A manifestation of Boltzmann's influence on Schrödinger is Schrödinger's enthusiastic quotation of Boltzmann's line of thought:

<sup>&</sup>lt;sup>6</sup>L. Boltzmann: Über irreversible Strahlungsvorgänge II., Berliner Ber. (1897) 1016–1018.

<sup>&</sup>lt;sup>7</sup>L. Boltzmann: Weitere Studien über das Wärmegleichgewicht unter Gasmolekülen, Sitzungsber. Kais. Akad. Wiss. Wien Math. Naturwiss. Classe **66** (1872) 275–370.

<sup>&</sup>lt;sup>8</sup>W. Ostwald: Lebenslinien – Eine Selbstbiographie, Klasing, Berlin 1927, vol. 2 p. 187 and 188.

"His line of thought may be called my first love in science. No other has ever thus enruptured me or will ever do so again." 9

Finally I would like to mention that Boltzmann in his lectures on Natural Philosophy in 1903 at the University of Vienna as well as in the second volume of his textbook on classical mechanics already anticipated the equal treatment of space coordinates and time which is introduced in the special theory of relativity. Furthermore in the lectures of Boltzmann and of his successor Fritz Hasenhrl in Vienna the students learned already about noneuclidean geometry, so that they could immediately start to work in this field when Einstein's general theory of relativity had been formulated. A result of this work was, for instance, the paper by Hans Thirring and Josef Lense<sup>10</sup> on the effects of the rotation of the earth on the moon and on satellites.

<sup>&</sup>lt;sup>9</sup>E. Schrödinger, S.B. Preuss. Akad. Wiss. Berlin (1929), pp. C–CII; reprinted in E. Schrdinger, Science Theory and Man, (New York: Dover 1957), p. XII.

<sup>&</sup>lt;sup>10</sup>H. Thirring and J. Lense: Über den Einfluß der Eigenrotation der Zentralkörperauf die Bewegung der Planeten und Monde nach der Einsteinschen Gravitationstheorie, Phys. Zeitschrift, Leipzig Jg.19 (1918), No. 8, p. 204–205.